

Rotational Barriers of Disilane, Hexafluorodisilane, and Hexamethyldisilane: *Ab Initio*, Density Functional, and Molecular Mechanics (MM3) Studies

SOO GYEONG CHO,¹ ONE KWON RIM,¹ GYOOSoon PARK²

¹Agency for Defense Development, P.O. Box 35-1, Yuseong, Taejeon 305-600, Korea

²Department of Chemistry, Kookmin University, Seoul 136-702, Korea

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ABSTRACT: We investigated structures, vibrational frequencies, and rotational barriers of disilane (Si_2H_6), hexafluorodisilane (Si_2F_6), and hexamethyldisilane (Si_2Me_6) by using *ab initio* molecular orbital and density functional theories. We employed four different levels of theories (i.e., HF/6-31G*, MP2/6-31G*, BLYP/6-31G*, and B3LYP/6-31G*) to optimize the structures and to calculate the vibrational frequencies (except for Si_2Me_6 at MP2/6-31G*). MP2/6-31G* calculations reproduce experimental bond lengths well, while BLYP/6-31G* calculations largely overestimate some bond lengths. Vibrational frequencies from density functional theories (BLYP/6-31G* and B3LYP/6-31G*) were in reasonably good agreement with experimental values without employing additional correction factors. We calculated the $\Delta G^\ddagger(298\text{ K})$ values of the internal rotation by correcting zero-point vibration energies, thermal vibration energies, and entropies. We performed CISD/6-31G*//MP2/6-31G* calculations and found the $\Delta G^\ddagger(298\text{ K})$ values for the internal rotation of Si_2H_6 , Si_2F_6 , and Si_2Me_6 to be 1.36, 2.06, and 2.69 kcal/mol, respectively. The performance of this level was verified by using G2 and G2(MP2) methods in Si_2H_6 . According to our theoretical results, the $\Delta G^\ddagger(298\text{ K})$ values were marginally greater than the $\Delta E^\ddagger(0\text{ K})$ values in Si_2F_6 and Si_2Me_6 due to the contribution of the entropy. In Si_2H_6 the $\Delta E^\ddagger(0\text{ K})$ and $\Delta G^\ddagger(298\text{ K})$ values were coincidentally similar due to a cancellation of two opposing contributions between zero-point and thermal vibrational energies, and entropies. Our calculated

Correspondence to: S. G. Cho

ΔG^\ddagger (298 K) values were in good agreement with experimental values published recently. In addition, we also performed MM3 calculations on Si_2H_6 and Si_2Me_6 . MM3 calculated rotational barriers and thermodynamic properties were compared with high level *ab initio* results. Based on this comparison, MM3 calculations reproduced high level *ab initio* results in rotational barriers and thermodynamic properties of Si_2H_6 derivatives including vibrational energies and entropies, although large errors exist in some vibrational frequencies.
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Introduction

It is well known that the rotational barriers of disilane (Si_2H_6) derivatives are notably smaller than those of corresponding carbon analogs.¹ For instance, the rotational barrier of disilane is 1.2 kcal/mol,² whereas in ethane it is 2.9 kcal/mol.^{3,4} This attenuation comes from a relatively longer Si—Si bond length.⁵ Schleyer and coworkers systematically investigated the relationship between the central bond lengths and rotational barriers and found that the rotational barrier becomes smaller due to poorer orbital overlap.⁵

However, the magnitudes¹⁰ of rotational barriers of Si_2H_6 derivatives remain controversial. For example, the rotational barrier of hexamethyldisilane (Si_2Me_6) was measured as 5.7 kcal/mol from NMR experiments in the solid state,⁶ and Allinger and coworkers developed the C—Si—Si—C torsional parameter of MM2 to reproduce this barrier.⁷ Another early molecular mechanics (MM) study performed by Mislow et al. reported that the rotational barrier of Si_2Me_6 was 1.05 kcal/mol,⁸ which was not accompanied by either experimental results or high level *ab initio* calculations at that time. Later the low rotational barrier of Si_2Me_6 was strongly supported by *ab initio* results. Profeta and colleagues⁹ utilized MP3/6–31G*//HF/3–21G(*) calculations and found the rotational barrier of Si_2Me_6 to be only 1.07 kcal/mol. This result has further been confirmed by Schleyer and coworkers.⁵ They utilized MP2/6–31G*//HF/6–31G* calculations to predict this barrier to be 1.05 kcal/mol. Thus, Schleyer et al. concluded that the substitution of methyl and other similar size groups to Si_2H_6 does not increase the rotational barrier at all. Recent reinvestigation of NMR experiments by Aksnes and Kimtys¹⁰ cast doubts on the assignments of previous experiments⁶ and

found this barrier to be 1.64–1.69 kcal/mol.¹⁰ Although this result is still slightly higher than *ab initio* values, the agreement between experiments and theories is much closer.

There has also been controversy regarding the rotational barrier of hexafluorodisilane (Si_2F_6). An early electron diffraction (ED) experiment suggested that the rotational barrier of Si_2F_6 is 0.5–0.7 kcal/mol.¹¹ On the other hand, recent gas phase Raman spectroscopy measured this barrier to be 1.5 kcal/mol,¹² which is about 1 kcal/mol higher than the previous ED result. Theoretical studies performed by Mastryukov et al.¹³ showed that HF/6–31G* results predict the rotational barrier of Si_2F_6 to be 0.75 kcal/mol, which is close to the value measured by the early ED experiment. Stølevik and Bakken¹⁴ performed MM calculations and found the rotational barrier of Si_2F_6 to be 1.2 kcal/mol. MM results by Stølevik and Bakken were not confirmed by either experimental data or high level *ab initio* results.

The accurate magnitude of rotational barriers is of particular importance to resolve these controversies and it also helps for one to understand the effect of substituents by comparing them with the rotational barrier of Si_2H_6 . In addition, these values may serve as reference values for the X—Si—Si—X (X=C, H, and F) torsional parameters in MM programs. Many molecular modeling studies of various silicon compounds including silicon polymers rely heavily on these parameters.¹⁵ Therefore, to better understand the rotational barriers around the Si—Si bond and resolve the controversies about the magnitude of Si_2H_6 derivatives, we carried out high levels of theoretical studies by using both *ab initio* molecular orbital (MO) and density functional (DF) theories. Because most experimental measurements of rotational barriers are the free energy differences (ΔG^\ddagger), we carried out all the necessary steps to obtain the ΔG^\ddagger values from our theoretical results.

We performed frequency calculations, and have computed zero-point vibrational energy (ZPVE), thermal vibrational energy (TVE), and entropy at each conformation.

Computational Details

All MO calculations were carried out using the GAUSSIAN-94¹⁶ series of programs on a CRAY Y-MP computer. The 6-31G* basis set¹⁷ was used throughout all the calculations. Geometry optimizations were undertaken at four levels of theories: the Hartree-Fock (HF) theory, the second order Møller-Plesset perturbation theory (MP2)¹⁸ with the frozen core approximation, DF theory using Becke's gradient corrected exchange functional¹⁹ and Lee-Yang-Parr's gradient corrected correlation functional²⁰ (BLYP), and Becke's three-parameter hybrid HF/DFT method²¹ using Lee-Yang-Parr's correlational functional (B3LYP). Two conformers (i.e., staggered and eclipsed conformers) were considered under the restriction of D_{3d} and D_{3h} symmetries, respectively. The harmonic frequencies were calculated to confirm that the staggered conformer is a true minimum and the eclipsed conformer is a transition state. In addition, calculated frequencies were compared with those observed experimentally and were corrected to obtain accurate ZPVE and TVE at 298 K. Entropies (S°) at 298 K were also calculated and used without using any correction factor. Higher levels of the electron correlation effect were employed via MP3 and CISD methods at the MP2/6-31G* geometries. To inspect the reliability of our calculational results, the rotational barrier of Si_2H_6 was further checked by using G2²² and G2(MP2)²³ methods, which are generally accepted as providing accurate relative energies. MM calculations were carried out using MM3 programs²⁴ with all standard parameters implemented in the program.

Results and Discussion

STRUCTURES

As mentioned previously, we optimized the structures at four different levels of theories: HF/6-31G*, MP2/6-31G*, BLYP/6-31G*, and B3LYP/6-31G*. Calculated results are summarized in Table I along with experimental values.^{25,26} Comparisons made with experimental data show

that all the levels of theories predict the geometric parameters reasonably. Recently, Ma et al. investigated the systematic difference between an experimental bond length and the one obtained theoretically and devised an empirical formula to estimate this difference for each bond type.²⁷ On the basis of their results, the bond lengths calculated from high level *ab initio* methods (the r_e values) are approximately 0.01–0.03 Å shorter than the experimental bond lengths; the actual errors will be smaller than those shown in Table I. Among theories utilized in this study, MP2/6-31G* calculations appear to give excellent geometries. It also has to be pointed out that some of bond lengths at the BLYP/6-31G* level are overestimated. The Si—Si bonds in Si_2H_6 and Si_2Me_6 and the Si—F bond in Si_2F_6 are especially largely overestimated by ca. 0.04–0.05 Å. This problem seems to not be particularly confined to our case but is also reported in other types of molecules.²⁸ Calculated bond angles in Si_2H_6 and Si_2F_6 were in excellent agreement with experimental values observed by ED. On the other hand, relatively large deviations (ca. 2°) in the bond angles of Si_2Me_6 were observed. However, we must mention that all the calculated bond angles of Si_2Me_6 agreed well among different levels of theories.

The structures of these compounds were examined previously by using theoretical tools. Leszczński et al. utilized respectably high levels of theories, including the CCSD(T) and CISD levels of theories using the TZP(f) basis set to probe the geometry of Si_2H_6 .²⁹ The Si—Si and Si—H bond lengths of Si_2H_6 calculated at the CCSD(T)/TZP(f) level were about 0.01 Å shorter than those from our MP2/6-31G* calculations, and bond angles were almost identical to our results. Mastryukov and colleagues investigated the geometric changes of Si_2H_6 and Si_2F_6 due to the rotation of the Si—Si bond.¹³ They employed HF/6-311G** calculations for Si_2H_6 and HF/6-31G* calculations for Si_2F_6 . The HF/6-311G** calculated Si—Si bond length of Si_2H_6 was predicted to be 2.364 Å, which was about 0.03 longer than the experimental value. Surprisingly, the performance of HF/6-311G** became slightly worse than that of HF/6-31G* in the prediction of the Si—Si bond length, although it improved the Si—H bond length somewhat. When the geometries between staggered and eclipsed conformations were compared, the change was negligible. Our results shown in Table I are in good agreement with the results by Mastryukov et al.¹³

TABLE I.
Calculated^a and Observed Geometries^b of Si₂H₆, Si₂F₆, and Si₂Me₆.

	MO Theories				MM3	Experiment
	SCF	MP2	BLYP	B3LYP		
Si ₂ H ₆ : staggered conformation ^c						
Si—Si	2.352	2.339	2.365	2.350	2.330	2.331 (3)
Si—H	1.478	1.487	1.499	1.489	1.486	1.492 (3)
∠Si—Si—H	110.43	110.40	110.72	110.62	109.88	110.3 (4)
∠H—Si—H	108.50	108.53	108.19	108.30	109.06	108.6 (4)
Eclipsed conformation						
Si—Si	2.362	2.350	2.376	2.361	2.330	
Si—H	1.478	1.487	1.498	1.489	1.486	
∠Si—Si—H	110.58	110.61	110.95	110.83	109.89	
∠H—Si—H	108.34	108.31	107.96	108.08	109.05	
Si ₂ F ₆ : staggered conformation ^d						
Si—Si	2.317	2.311	2.331	2.319		2.317 (6)
Si—F	1.570	1.596	1.608	1.592		1.564 (2)
∠Si—Si—F	110.74	110.43	110.48	110.53		110.32
∠F—Si—F	108.17	108.49	108.45	108.39		108.6 (3)
Eclipsed conformation						
Si—Si	2.322	2.317	2.340	2.327		
Si—F	1.570	1.596	1.608	1.592		
∠Si—Si—F	110.81	110.51	110.60	110.63		
∠F—Si—F	108.10	108.41	108.32	108.29		
Si ₂ Me ₆ : staggered conformation ³						
Si—Si	2.370	2.350	2.388	2.367	2.331	2.340 (7)
Si—C	1.902	1.897	1.919	1.905	1.884	1.877 (3)
C—H	1.087	1.095	1.104	1.097	1.112	1.127 (9)
∠Si—Si—C	110.47	110.40	110.63	110.53	109.19	108.4 (4)
∠C—Si—C	108.46	108.52	108.28	108.39	109.75	110.3 (8)
∠Si—C—H	111.44	111.23	111.36	111.34	110.22	108.7 (8)
∠H—C—H	107.43	107.66	107.52	107.54	108.71	110.3 (8)
Eclipsed conformation						
Si—Si	2.382	2.363	2.399	2.381	2.334	
Si—C	1.902	1.897	1.919	1.905	1.885	
C—H	1.087	1.095	1.104	1.097	1.112	
∠Si—Si—C	110.69	110.62	110.71	110.62	109.46	
∠C—Si—C	108.22	108.30	108.20	108.30	109.48	
∠Si—C—H	111.45	111.23	111.38	111.35	110.23	
∠H—C—H	107.42	107.65	107.50	107.52	108.70	

^aUsing the 6-31G* basis set.
^bUnits are Å for bond lengths and degrees for bond angles.
^cExperimental data from electron diffraction (ED, gas phase), ref. 25.
^dExperimental data from ED (*r*_a⁰ value, gas phase), ref. 11.
^eExperimental data from ED (*r*_g value, gas phase), ref. 26.

VIBRATIONAL FREQUENCIES

Our main intention to calculate vibrational frequencies was for the accurate corrections of ZPVE and TVE. *Ab initio* theories are known to overestimate vibrational frequencies.³⁰ Thus, we performed these corrections by comparing them with experimental frequencies. Although Rauhut and Pulay advocated the use of multiple scaling factors according to different types of internal coordi-

nates,³¹ the overall scaling that we employed in this study is also used commonly, and is, in fact, easy to handle. Our calculated vibrational frequencies of Si₂H₆, Si₂F₆, and Si₂Me₆ are shown in Table II along with experimental values. Because experimental vibrational frequencies of all three compounds were measured, the calculated vibrational frequencies at various levels of theories were compared with available experimental data and

TABLE II. Comparison of Calculated^a and Observed Vibrational Frequencies^b of Si₂H₆, Si₂F₆, and Si₂Me₆.

	MO Theory				MM3	Experiment	Symmetry
	SCF	MP2	BLYP	B3LYP			
Si ₂ H ₆ ^c	2376	2303	2173	2239	2129	2163	A _{1g}
	2370	2316	2191	2252	2163	2179	E _u
	2361	2308	2180	2242	2162	2155	E _g
	2360	2293	2165	2230	2128	2154	A _{2u}
	1042	987	932	958	972	940	E _u
	1033	966	904	932	800	920	A _{1g}
	1026	971	918	944	970	941	E _g
	948	888	832	857	806	844	A _{2u}
	697	663	621	640	600	628	E _g
	465	452	416	433	428	432	A _{1g}
	417	385	374	383	550	379	E _u
	132	140	133	135	146	—	A _{1u}
Si ₂ F ₆ ^d	1066	1018	970	1007		992	E _u
	1056	1001	964	1000		979	E _g
	985	931	878	916		915	A _{1g}
	881	833	791	825		824	A _{2u}
	593	564	520	544		545	A _{1g}
	426	401	378	392		406	A _{2u}
	361	342	323	334		340	E _g
	324	307	291	301		310	E _u
	237	225	208	217		218	A _{1g}
	212	197	183	191		203	E _g
	113	101	91	97		153	E _u
	26	27	18	23		—	A _{1u}
Si ₂ Me ₆ ^e	3253		3032	3115	2982	2956	E _g
	3253		3032	3114	2982	2958	E _u
	3252		3032	3114	2981	— ^f	A _{1u}
	3250		3025	3108	2982	2956	A _{1g}
	3250		3031	3113	2981	— ^f	A _{2g}
	3249		3024	3108	2982	2958	A _{2u}
	3247		3023	3106	2982	2958	E _u
	3246		3023	3106	2982	2956	E _g
	3185		2960	3038	2879	2901	A _{1g}
	3183		2959	3037	2879	2902	A _{2u}
	3183		2958	3037	2879	2902	E _u
	3183		2958	3037	2879	2901	E _g
	1621		1477	1511	1420	1442	A _{2u}
	1618		1476	1510	1420	1441	A _{1G}
	1616		1471	1506	1421	1441	E _g
	1611		1464	1500	1421	1442	E _u
	1606		1458	1493	1420	— ^f	A _{1u}
	1604		1457	1492	1418	1418	E _g
	1603		1459	1493	1418	1417	E _u
	1599		1451	1486	1419	— ^f	A _{2g}
	1460		1298	1336	1272	1263	A _{1g}
	1454		1293	1330	1271	1255	A _{2u}

TABLE II.
(Continued)

	MO Theory				MM3	Experiment	Symmetry
	SCF	MP2	BLYP	B3LYP			
	1448		1282	1321	1274	1251	E _u
	1446		1281	1319	1273	1254	E _g
	996		903	927	917	885	A _{1g}
	943		861	882	910	828	E _u
	939		855	876	911	800	E _g
	933		849	870	911	828	A _{2u}
	845		767	786	882	757	E _g
	799		726	743	882	722	E _u
	756		685	701	879	— ^f	A _{1u}
	753		686	701	879	— ^f	A _{2g}
	730		663	688	744	690	E _u
	724		656	681	746	698	E _g
	666		600	625	652	638	A _{1g}
	633		572	596	631	608	A _{2u}
	424		376	393	388	404	A _{1g}
	259		235	241	245	245	E _g
	254		235	239	255	242	A _{2u}
	214		197	202	227	212	E _u
	187		179	180	197	—	E _g
	181		170	171	175	175	A _{1g}
	176		166	168	191	212	E _u
	170		160	163	183	175	E _g
	164		167	166	191	— ^f	A _{1u}
	159		150	152	185	— ^f	A _{2g}
	96		97	94	130	94	E _u
	22		13	14	28	— ^f	A _{1u}

^aUsing the 6-31G* basis set.
^bFrequencies are per centimeter.
^cExperimental data from ref. 2.
^dExperimental data from ref. 12.
^eExperimental data from 32.
^fInactive.

we attempted to fit calculated frequencies linearly by using a scaling factor. The unsigned average errors and optimum scaling factors are compiled in Table III.

Through our fitting, the magnitude of optimum scaling factors appears to be quite common in Si₂H₆ and Si₂Me₆. For instance, the optimum scaling factors for SCF frequencies in Si₂H₆ and Si₂Me₆ are 0.911 and 0.905, respectively, and the one for MP2 frequencies in Si₂H₆ is 0.941. However, the optimum scaling factor for Si₂F₆ is much higher than the usual one, probably because all vibrational frequencies are shifted significantly toward a lower region. We also calculated vibrational frequencies with DF theories. Previous reports were given that vibrational frequencies from DF theo-

ries, especially BLYP and B3LYP, are in excellent agreement with the experimental ones with a scaling factor that is close to unity.^{31,33} Our results can be added as another example following this general trend. After calculated frequencies were adjusted with the optimum scaling factor, the unsigned average errors from experimental frequencies were approximately 10–15 cm⁻¹, except SCF frequencies in Si₂Me₆.

Accurate prediction of calculated frequencies is also reflected to vibrational energies. Scaled ZPVEs and TVEs are almost the same among different levels of theories (within 0.1 kcal/mol). One exception was found that the ZPVE and TVE of Si₂Me₆ at the SCF level were 0.4 kcal/mol higher than those calculated from DF theories. However,

TABLE III.
Unsigned Average Errors^a of Calculated
Frequencies of Si₂H₆, Si₂F₆, and Si₂Me₆ Using
Different Levels of Theories.

	MO Theories ^b				
	SCF	MP2	BLYP	B3LYP	MM3
Si ₂ H ₆ : unsigned errors					
Unscaled	124.1	73.1	13.9	34.8	45.3
Scaled	8.7	10.7	12.8	12.3	43.6
	(0.911) ^c	(0.941)	(0.997)	(0.968)	(1.006)
Si ₂ F ₆ : unsigned errors					
Unscaled	41.1	15.1	26.4	12.6	
Scaled	8.7	10.8	14.0	13.0	
	(0.932)	(0.983)	(1.036)	(0.996)	
Si ₂ Me ₆ : unsigned errors					
Unscaled	147.2	—	36.7	67.1	32.5
Scaled	25.7	—	14.3	14.2	30.4
	(0.905)		(0.979)	(0.954)	(0.999)

^aUnits are percentometer.

^bUsing the 6-31G* basis set.

^cValues in parentheses are scaling factors for the least square fit of experimental frequencies.

this difference was also canceled out when the differences of ZPVE and TVE between staggered and eclipsed conformations were taken.

ROTATIONAL BARRIERS

The magnitude of rotational barriers can be defined as the free energy difference between staggered and eclipsed conformations. The staggered conformation should be a minimum, while the eclipsed conformation is a transition state. This can be verified by calculating vibrational frequencies. The staggered conformations with D_{3d} symmetry of three compounds were truly confirmed to be a minimum with no negative eigenvalue, while the eclipsed conformations with D_{3h} symmetry of all three compounds were a transition state with only one negative eigenvalue.³⁴

While experimental values were furnished as ΔE[‡], ΔH[‡], and ΔG[‡] values according to which experiments were performed depending upon experimental natures, theoretical results (without any thermodynamic correction) provided ΔE[‡](0 K). Thermodynamic corrections from theoretical values enabled us to obtain the ΔH[‡] and ΔG[‡] values. For ZPVE and TVE corrections we used scaling factors given in Table III, which were obtained from the comparison with experimental vibrational frequencies. Entropy corrections were made

by using unscaled frequencies, because calculated entropies from unscaled frequencies are known to reproduce experimental values well in various simple molecules.³⁵ The rotational barriers calculated at various levels are summarized in Table IV along with the values observed experimentally. Our values seem to be remarkably similar among the levels of theories we employed in this study. Thus, electron correction may little affect the magnitude of rotational barriers in these particular compounds.

For Si₂H₆ the ΔG[‡](298 K) value for the internal rotation is 1.36 kcal/mol at the CISD/6-31G*//MP2/6-31G* level. We further extended our calculations by utilizing the G2 and G2(MP2) methods to examine whether our calculational levels properly compute rotational barriers of Si₂H₆ derivatives. The G2 and G2(MP2) methods predict rotational barrier of Si₂H₆ to be 1.53 and 1.56 kcal/mol, respectively. When our CISD/6-31G*//MP2/6-31G* calculations were compared with the experimental value (1.26 kcal/mol) and the G2 and G2(MP2) results, they appear to furnish excellent values of rotational barriers and thermodynamic corrections in Si₂H₆ derivatives. Several previous theoretical results, which are in fact ΔE[‡](0 K), also were in good agreement with experimental data. If the ΔH[‡](298 K) value is taken to compare with the experimental value, it is obviously too low. Finally, when the ΔG[‡](298 K) value is computed by correcting the entropy, the rotational barrier goes up to 1.36 kcal/mol. These values are quite close to the uncorrected ΔE[‡](0 K) value. Thus, the agreement of the rotational barrier of Si₂H₆ to the experimental one is probably due to a fortuitous cancellation of two opposing effects: the effects of ZPVE and TVEs and the entropy effect.

The magnitude of rotational barrier of Si₂F₆ is controversial. Early ED measured it as 0.51–0.73 kcal/mol.¹¹ But recent Raman experiments presented a much higher value of 1.57 kcal/mol.¹² Because both experiments attempted to fit V₃ terms, these values were assumed to be a ΔE[‡] value. However, the discrepancy between two different magnitudes is quite confusing. Our calculated ΔE[‡](0 K) values are 0.76 kcal/mol at CISD/6-31G*//MP2/6-31G*, which is close to earlier ED results by Oberhammer.¹¹ If the rotational barrier of Si₂F₆ is corrected to the ΔH[‡](298 K) value, the value is notably reduced to be only 0.16 kcal/mol. Further correction to ΔG[‡](298 K) finally increases the rotational barrier of Si₂F₆ to 2.06 kcal/mol. In contrast to Si₂H₆, the entropy effect

TABLE IV.
Calculated Rotational Barriers of Si₂H₆, Si₂F₆, and Si₂Me₆ Along with Observed Values.

	MO Theories ^a								Experimental Data	
	SCF	MP2	BLYP	B3LYP	MP3 ^b	CISD ^b	G2	G2(MP2)		
Si ₂ H ₆										
ΔE [‡] (0 K) ^c	0.95	1.07	0.87	0.91	1.04	1.01			1.19	1.26 (3) ^f
ΔH [‡] (0 K) ^d	0.86	0.97	0.85	0.81	0.94	0.91	1.00	1.04	0.91	
ΔH [‡] (298 K) ^d	0.39	0.50	0.39	0.34	0.47	0.44	0.52	0.56	0.51	
ΔG [‡] (298 K) ^e	1.33	1.42	1.33	1.27	1.39	1.36	1.53	1.56	1.31	
Si ₂ F ₆										
ΔE [‡] (0 K) ^g	0.77	0.75	0.71	0.74	0.74	0.76				1.57 ^h , 0.51–0.73 ⁱ
ΔH [‡] (0 K)	0.74	0.72	0.70	0.72	0.71	0.73				
ΔH [‡] (298 K)	0.18	0.15	0.12	0.14	0.14	0.16				
ΔG [‡] (298 K)	2.06	2.05	2.28	2.14	2.04	2.06				
Si ₂ Me ₆										
ΔE [‡] (0 K) ^j	0.96	1.05	1.02	0.94	1.05	1.05			1.21	1.64–1.67, ^l 5.7 ^m
ΔH [‡] (0 K)	1.04	1.13 ^k	0.96	0.90	1.13	1.13			1.16	
ΔH [‡] (298 K)	0.41	0.50 ^k	0.41	0.33	0.50	0.50			0.55	
ΔG [‡] (298 K)	2.60	2.69 ^k	2.60	2.51	2.69	2.69			2.63	

^aUnits in kilo calories / mole. All the theories used the 6–31G* basis set, except G2 and G2(MP2). For the basis sets and theoretical levels used in G2 and G2(MP2) methods, see refs. 22 and 23, respectively.
^bSingle point calculations at the MP2/6–31G* geometries. All the correction terms are based on MP2/6–31G* frequency calculations.
^cAbsolute energy (unit: hartree) for staggered conformation is –581.3050942 (SCF), –581.464711 (MP2), –582.5068537 (BLYP), –582.5827425 (B3LYP), –581.4976238 (MP3), and –581.4911511 (CISD).
^dScaled for experimental frequencies. Scale factors shown in Table III are used for all 3 compounds.
^eEntropies are not scaled.
^fFrom Raman (gas phase), ref. 2.
^gAbsolute energy (unit: hartree) for staggered conformation is –1174.8802559 (SCF), –1176.1431612 (MP2), –1178.3276738 (BLYP), –1178.4150427 (B3LYP), –1176.0556305 (MP3), and –1175.8559146 (CISD).
^hFrom Raman (gas phase), ref. 11.
ⁱFrom electron diffraction, ref. 10.
^jAbsolute energy (unit: hartree) for staggered conformation is –815.5784756 (SCF), –816.5352958 (MP2), –818.2923109 (BLYP), –818.5365582 (B3LYP), –816.6253431 (MP3), and –816.394006 (CISD).
^kUsed SCF frequency calculations.
^lFrom ¹H and ¹³C spin-lattice relaxation time measurements in the solid state (from 155 K to 285K), ref. 10.
^mFrom ¹H spin-lattice relaxation time measurements in solid states from solid-state NMR, ref. 6.

of Si₂F₆ appears to surpass opposing effects of ZPVE and TVEs. The experimental values of rotational barrier in Si₂Me₆ were more confusing, as discussed in the Introduction. Early NMR experimental measurement was 5.7 kcal/mol⁶ but recent reinvestigation by Aksnes and Kimtys provided a significantly lower value of 1.6–1.7 kcal/mol,¹⁰ with an argument about the assignment in previous experimental data. *Ab initio* calculations predict the rotational barrier of Si₂Me₆ to be only ca. 1 kcal/mol.^{5,8} *Ab initio* theoretical results strongly support the experimental value by Aksnes and Kimtys but are still slightly lower by more than 0.5 kcal/mol. When we repeated the calculations, our ΔE[‡](0 K)

values were essentially the same as previous *ab initio* works. However, the rotational barrier became 2.5–2.7 kcal/mol when the values were corrected to obtain the ΔG[‡](298 K) value. Our calculated ΔG[‡](298 K) value was higher than the experimental values by approximately 1 kcal/mol. There may be several reasons for this discrepancy. Because these experiments were performed in the solid state, these values may not be an appropriate reference for our theoretical studies. On the other hand, these experiments were performed at various temperatures ranging from 155 to 285 K and were computed from regression fitting. Our calculated ΔG[‡] values were changed substantially due to the change of the temperature. For instance,

ΔG^\ddagger became 1.75 kcal/mol at 150 K, 1.96 kcal/mol at 180 K, and 2.02 kcal/mol at 220 K. Because the experimental value is considered an average value in the temperature range from 155 to 285 K, our calculated ΔG^\ddagger value seems to be in good agreement with the experimental value.

Substitutions in Si_2H_6 appear to raise rotational barriers due to the entropy effect. Rotational barriers obtained from many previous theoretical studies were compared with experimental data by using either uncorrected $\Delta E^\ddagger(0 \text{ K})$ values or $\Delta H^\ddagger(0 \text{ K})$ values with only ZPVE correction. In fact, these values are usually in good agreement with experimental values in a variety of small molecules.^{1,36} Our study may suggest that this is a coincidence that comes from an opposite trend between the effect of ZPVE and TVEs and the entropy effect. On the other hand, in highly substituted compounds such as Si_2Me_6 , rotational barriers measured experimentally may differ considerably from the $\Delta E^\ddagger(0 \text{ K})$ value obtained theoretically due to a large entropy effect.

REMARKS ON MM3 RESULTS

In contrast to MO calculations, MM results largely depend on the reference values with which the parameters were developed. If the MM parameter was developed on the basis of experimental results, the MM calculated rotational barrier can simulate the $\Delta G^\ddagger(298 \text{ K})$ value. On the other hand, the MM calculated barrier reproduces the *ab initio* calculated $\Delta E^\ddagger(0 \text{ K})$ value if the MM parameter was developed from *ab initio* results without any thermodynamic correction. Quite often *ab initio* calculations supplement experimental data in the development of MM force field parameters. However, the use of different thermodynamic values from different methodologies, besides the intrinsic errors present in each value, may cause profound errors in the process of parameterization. Thus, it is quite important for one to clarify which thermodynamic values were reported in each experiment or calculation.

In contrast to MM2, MM3 now can calculate vibrational frequencies and thermodynamic properties.²⁴ Thus, one can obtain the $\Delta G^\ddagger(298 \text{ K})$ value for the internal rotation from MM3 results. To do this, additional calculational steps should be required to correct ZPVEs, TVEs, and entropy. If we follow this scheme to obtain the $\Delta G^\ddagger(298 \text{ K})$ value for the internal rotation, MM3 torsional parameters should be developed to reproduce the $\Delta E^\ddagger(0 \text{ K})$ value. If MM3 torsional potentials simulate the

$\Delta G^\ddagger(298 \text{ K})$ value, further thermodynamic corrections may lead to erroneous value. Thus, extreme care in utilizing exact thermodynamic values in the development of MM parameters should be taken, as mentioned previously. Calculation of the $\Delta G^\ddagger(298 \text{ K})$ value can be a remedy for one of the well-known shortcomings in MM2 results, that is, that rotational barriers of highly congested molecules are profoundly low.^{37–39} Lii and Allinger demonstrated that MM3 calculated rotational barriers of highly congested hydrocarbons are improved considerably by calculating the $\Delta G^\ddagger(298 \text{ K})$ value.^{24b} This improvement was further confirmed in a recently developed MM4 force field.⁴⁰ Previously, we also noticed that *ab initio* calculated rotational barriers were also seriously smaller than the experimental values in highly crowded silicon compounds⁴¹ if the $\Delta E^\ddagger(0 \text{ K})$ value was used. Acquiring the $\Delta G^\ddagger(298 \text{ K})$ value appears to be essential in both *ab initio* and MM calculations in order to properly predict the rotational barriers of highly crowded molecules. We felt that it would be quite interesting to see whether MM3 calculations could reproduce high level *ab initio* results in rotational barriers and thermodynamic properties of these compounds. Thus, we performed MM3 calculations on these compounds, except Si_2F_6 , whose MM parameters are not available yet.

Our MM calculated geometries of Si_2H_6 and Si_2Me_6 are shown in Table I. In general, geometries were in excellent agreement with those obtained by either experiments or high level *ab initio* calculations. One of the interesting features shown in MM3 calculated geometric parameters is that the geometric parameters seem to be near invariant due to conformational changes. Vibrational frequencies of Si_2H_6 and Si_2Me_6 calculated from MM3 are shown in Table II, and average errors of MM3 calculated vibrational frequencies from experimental values are summarized in Table III. While most frequencies are in excellent agreement with the experimental ones, some of them show large discrepancies from experimental data. These errors may come from the absence of certain force fields in MM3, as explained by Allinger and colleagues.^{24b,40} Because there have been continual efforts to improve the accuracy of MM calculated vibrational frequencies,⁴⁰ we believe that errors of MM calculated vibrational frequencies will be reduced significantly in future force fields. The differences of some vibrational frequencies cause considerable errors of MM3 calculated ZPVEs, when compared with those from *ab initio* calculations. However, the errors are canceled out when

the MM3 calculated ZPVE differences between eclipsed and staggered conformations are considered.

The rotational barriers of Si_2H_6 and Si_2Me_6 , which are taken directly from MM3 steric energies, are 1.19 and 1.21 kcal/mol, respectively (see Table IV). Surprisingly, the rotational barrier of Si_2Me_6 appears to be readjusted since the initial development with MM2, in which the barrier has been reported to be 5.77 kcal/mol.^{7,42} Although MM3 calculated barriers taken from MM3 steric energies without any further corrections may represent either $\Delta E^\ddagger(0\text{ K})$ or $\Delta G^\ddagger(298\text{ K})$ value depending upon reference data, fitting to the $\Delta E^\ddagger(0\text{ K})$ value will be more suitable with the thermodynamic correction scheme. We actually performed these corrections under the assumption that MM3 calculates the $\Delta E^\ddagger(0\text{ K})$ values. As shown in Table IV, thermodynamic corrections with the MM3 program are in good agreement with high level *ab initio* results. We feel that this example may help to solve the controversies about the rotational barriers in highly congested systems. In general, the rotational barriers of highly congested compounds (i.e., hexamethylethane) have been known to be calculated as low by transferring force field parameters from simple compounds.^{37,38} The entropy effect is suggested to cause this controversy.³⁸ Thus, the calculation of thermodynamic properties including entropy is probably essential to obtain accurate barriers of highly congested compounds. We are planning to examine these systems with both *ab initio* and MM calculations.

Conclusions

We investigated the structures, vibrational frequencies, and rotational barriers of Si_2H_6 , Si_2F_6 , and Si_2Me_6 by using high level *ab initio* MO and DF theories. Not surprisingly, MP2/6-31G* performs better than other theories in the prediction of the structures of Si_2H_6 derivatives. BLYP/6-31G* overestimates some bond lengths notably. DF theories, both BLYP/6-31G* and B3LYP/6-31G*, reproduce the vibrational frequencies well without employing further correction factors.

We calculated the $\Delta G^\ddagger(298\text{ K})$ values for the internal rotation in order to compare them directly with experimental data available. Calculated $\Delta E^\ddagger(0\text{ K})$, $\Delta H^\ddagger(0\text{ K})$, $\Delta H^\ddagger(298\text{ K})$, and $\Delta G^\ddagger(298\text{ K})$ values were nearly the same among the various levels

of theories we employed in this study, that is, HF/6-31G*, MP2/6-31G*, BLYP/6-31G*, and B3LYP/6-31G*. Our best estimates for the rotational barriers of Si_2H_6 , Si_2F_6 , and Si_2Me_6 , which was based on the $\Delta G^\ddagger(298\text{ K})$ value at the CISD/6-31G*//MP2/6-31G* level, were 1.36, 2.06, and 2.69 kcal/mol, respectively. Our values were in excellent agreement with the recent experimental data. The $\Delta G^\ddagger(298\text{ K})$ values of Si_2F_6 and Si_2Me_6 from our calculations were somewhat higher than the previous *ab initio* results with either an uncorrected $\Delta E^\ddagger(0\text{ K})$ value or a $\Delta H^\ddagger(0\text{ K})$ value with ZPVE corrections. On the other hand, the $\Delta G^\ddagger(298\text{ K})$ value for the internal rotation of Si_2H_6 was almost the same as the $\Delta E^\ddagger(0\text{ K})$ due to a cancellation of two opposing contributions between zero-point and thermal vibrational energies and entropies. MM3 calculations also required thermodynamic corrections to obtain precise rotational barriers of highly congested compounds. By testing Si_2H_6 derivatives, MM3 calculations provided good results in geometries, vibrational frequencies, and thermodynamic properties including the $\Delta G^\ddagger(298\text{ K})$ values for the internal rotation.

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